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# A nocturnal atmospheric loss of CH<sub>2</sub>I<sub>2</sub> in the remote marine boundary layer

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**Abstract** Ocean emissions of inorganic and organic iodine compounds drive the biogeochemical cycle of iodine and produce reactive ozone-destroying iodine radicals that influence the oxidizing capacity of the atmosphere. Di-iodomethane (CH<sub>2</sub>I<sub>2</sub>) and chloro-iodomethane (CH<sub>2</sub>ICl) are the two most important organic iodine precursors in the marine boundary layer. Ship-borne measurements made during the TORERO (Tropical Ocean tRoposphere Exchange of Reactive halogens and Oxygenated VOC) field campaign in the east tropical Pacific Ocean in January/February 2012 revealed strong diurnal cycles of CH<sub>2</sub>I<sub>2</sub> and CH<sub>2</sub>ICl in air and of CH<sub>2</sub>I<sub>2</sub> in seawater. Both compounds are known to undergo rapid photolysis during the day, but models assume no night-time atmospheric losses. Surprisingly, the diurnal cycle of CH<sub>2</sub>I<sub>2</sub> was lower in amplitude than that of CH<sub>2</sub>ICl, despite its faster photolysis rate. We speculate that night-time loss of CH<sub>2</sub>I<sub>2</sub> occurs due to reaction with NO<sub>3</sub> radicals. Indirect results from a laboratory study under ambient atmospheric boundary layer conditions indicate a  $k_{\text{CH}_2\text{I}_2+\text{NO}_3}$  of  $\leq 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; a previous kinetic study carried out at  $\leq 100$  Torr found  $k_{\text{CH}_2\text{I}_2+\text{NO}_3}$  of  $4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Using the 1-dimensional atmospheric THAMO model driven by sea-air fluxes calculated from the seawater and air measurements (averaging  $1.8 \pm 0.8 \text{ nmol m}^{-2} \text{ d}^{-1}$  for CH<sub>2</sub>I<sub>2</sub> and  $3.7 \pm 0.8 \text{ nmol m}^{-2} \text{ d}^{-1}$  for CH<sub>2</sub>ICl), we show that

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the model overestimates night-time  $\text{CH}_2\text{I}_2$  by >60 % but reaches good agreement with the measurements when the  $\text{CH}_2\text{I}_2 + \text{NO}_3$  reaction is included at  $2\text{--}4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We conclude that the reaction has a significant effect on  $\text{CH}_2\text{I}_2$  and helps reconcile observed and modeled concentrations. We recommend further direct measurements of this reaction under atmospheric conditions, including of product branching ratios.

**Keywords** di-iodomethane ·  $\text{NO}_3$  radical · Atmosphere · Ocean · Iodine

## 1 Introduction

The potential for tropospheric ozone destruction by iodine was recognized many decades ago (Chameides and Davis 1980) and confirmed later by measurements of the iodine oxide radical (IO) (Alicke et al. 1999; Read et al. 2008; Mahajan et al. 2010a, b; Gómez Martín et al. 2013; Großmann et al. 2013; Dix et al. 2013; Prados-Roman et al. 2015). A ubiquitous global marine boundary layer (MBL) background of around 0.5–1 pptv IO has been established by these measurements. The presence of IO establishes that active atmospheric iodine chemistry is occurring, driven by photochemical breakdown of iodine precursors. Iodine is a significant ozone-depleting agent in the MBL, being responsible for 20–30 % of the total ozone loss in that region (Saiz-Lopez et al. 2014; Prados-Roman et al. 2015; Sherwen et al. 2015). Calculations from global chemistry transport models indicate that globally iodine provides an odd oxygen ( $\text{Ox}$ ) loss of 12–16 % of the total, at around  $\sim 720 \text{ Tg yr}^{-1}$  (Saiz-Lopez et al. 2014; Sherwen et al. 2015).

Oceanic emissions of the inorganic gases  $\text{I}_2$  and HOI, produced from ozonolysis of surface iodide (Carpenter et al. 2013; MacDonald et al. 2014), are believed to contribute  $\sim 2\text{--}2.5 \text{ Tg I yr}^{-1}$ , around 80 % of global iodine emissions (Sherwen et al. 2015; Prados-Roman et al. 2015). However, in certain regions - including at high latitudes where surface ocean iodide levels are low, and in locations where wind speeds are high and surface ozone ( $\text{O}_3(\text{g})$ ) mixing ratios are relatively low - organic gases may contribute 50 % or more of the iodine source (Prados-Roman et al. 2015). There are few oceanic flux measurements of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$ , but available data suggest that they contribute  $\sim 0.11$  and  $0.17 \text{ Tg I yr}^{-1}$  to the global atmosphere (Jones et al. 2010) similar in total to methyl iodide ( $\text{CH}_3\text{I}$ ) emissions (Carpenter et al. 2014).

Both  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  are known to have short photolysis lifetimes in the atmosphere of  $\sim 5 \text{ min}$  and  $\sim 1 \text{ h}$  at midday in mid-latitudes, respectively (Rattigan et al. 1997; Roehl et al. 1997; Mössinger et al. 1998), leading to strong diurnal cycles (Carpenter et al. 1999; Jones et al. 2010). Photolysis is assumed to be the sole driver of atmospheric loss of these compounds, and in the presence of chloride ions likely dominates aqueous loss also (Jones and Carpenter 2005; Martino et al. 2005). Laboratory determination of the photolysis rates in  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  in seawater indicate aqueous lifetimes at midday in mid-latitudes of 9–12 min for  $\text{CH}_2\text{I}_2$  and 9–13 h for  $\text{CH}_2\text{ICl}$  (Jones and Carpenter 2005; Martino et al. 2005).

So far, the possibility of night-time losses of the di-halomethanes remains unexplored in terms of analysis of field data and atmospheric modeling. Nakano et al. (2006) performed a kinetic study of the atmospheric reaction of  $\text{NO}_3$  with  $\text{CH}_2\text{I}_2$  (reaction 1) and determined a rate

constant of  $(4.0 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This would result in a nocturnal lifetime of  $\sim 3 \text{ h}$  for  $\text{CH}_2\text{I}_2$  in the clean MBL.



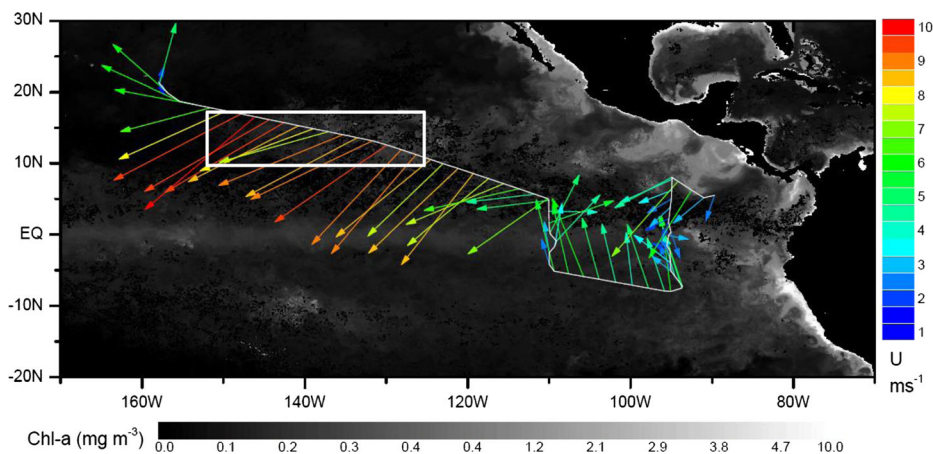
However this study was carried out at low pressure (25–100 Torr of  $\text{N}_2$  diluent) and there appear to be no corroborating studies in the literature.

Here we report seawater and air measurements and calculated ocean emissions of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  from the eastern tropical Pacific Ocean. We focus on a 4-day period of near constant sea surface temperatures, chlorophyll *a* levels, and wind speeds, whilst sampling water from the North Equatorial Current. Measurements are compared to the 1D Tropospheric Halogen Chemistry Model (THAMO) (Saiz-Lopez et al. 2008) to test understanding of the atmospheric losses of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$ . We also infer a range of possible values for  $k_{\text{CH}_2\text{I}_2+\text{NO}_3}$  from kinetic results obtained during a laboratory study of the reaction of the Criegee intermediate  $\text{CH}_2\text{OO}$  with  $\text{NO}_2$ , which are the first data (to our knowledge) for this reaction obtained under ambient atmospheric boundary layer conditions (Ouyang et al. 2013).

## 2 Methods

### 2.1 Cruise track and shipboard measurements

The NOAA research vessel *Ka'imimoana* sailed from Pearl Harbour, Hawaii to Puntarenas, Costa Rica, via the  $95^\circ\text{W}$  and  $110^\circ\text{W}$  Tropical Atmosphere Ocean (TAO) buoy lines from 27th Jan. until 28th Feb. 2012 (Fig. 1). Very short-lived halocarbons (VSLH) were quantified in air and seawater at regular intervals during the cruise.



**Fig. 1** Cruise track of the R/V *Ka'imimoana* during the TORERO cruise during Jan./Feb. 2012, superimposed on chlorophyll-*a* background (MODIS) and showing wind speed and direction. The white rectangle shows the part of the cruise track chosen for the case study

### 2.1.1 Halocarbon measurements

Air was sampled from the top of the 10 m bow tower through a 60 m sampling line (1/2" PFA, Swagelok). A diaphragm pump (KNF, NO35.1.2AN.18) was used to pull  $\sim 30 \text{ L min}^{-1}$  down the line. At 1 m before the diaphragm pump, a T-union connected approximately 50 cm of 1/4" heated instrument grade stainless steel line (Restek) to an inverted metal bellows pump (Senior Aerospace MB-158) which provided 10 psi of positive pressure to the instrument via  $\sim 1.5 \text{ m}$  of 1/8" heated instrument grade stainless steel tubing with a pressure relief valve maintaining flow and draining any water whilst the instrument was not sampling. An ozone analyser (Thermo Scientific Model 49i) drawing  $3 \text{ L min}^{-1}$  was also connected downstream of the metal bellows pump. Water was removed from the sample stream using a Nafion drier (Permapure, MD-050-72S-2) with a nitrogen counter current.

The absence of any line losses of VSLH using 100 m of 1/2" PFA sampling line was verified in laboratory tests. A 35 L electropolished cylinder (Essex Cryogenics) was filled with ambient air at 60 bar using a clean, high-pressure compressor (RIX SA-6). The cylinder air was (1) introduced directly into the instrument, using a pressure regulator and (2) used to over-flow the inlet of the pumped sampling system using 100 m of PFA line. This was performed at an open T-union so as not to influence the pressure in the sample line. The results of multiple analyses of air introduced directly and through the pumped sample line were compared and showed no significant losses (deviations less than the instrument reproducibility) for all of the halocarbons measured.

Calibrations were run daily using 1 L of a National Oceanic and Atmospheric Administration (NOAA) VSLH standard (SX-3570). All analytes in this standard were tested to be stable over 4 years by comparison with subsequently prepared standards, SX-3576 and SX-3581 at 2 and 4 years, respectively. In order to correct for short-term sensitivity changes between calibrations, atmospheric  $\text{CCl}_4$  was used as an internal standard. The air samples ( $1 \text{ L}$  at  $100 \text{ mL min}^{-1}$ ), calibration and zero (nitrogen,  $\text{n6.0}$ ) gas streams were selected (Markes, CIA8) and pre-concentrated on a cooled absorbent trap at  $-30^\circ \text{C}$  (Markes, Unity2). Samples were desorbed at  $300^\circ \text{C}$  onto a gas chromatograph (GC, Agilent 7890) and separated on a capillary column (Restek, RTX502.2,  $30 \text{ m}$ ,  $0.25 \text{ mm ID}$ ,  $1.25 \mu\text{m}$ ) using an oven temperature ramp ( $40\text{--}250^\circ \text{C}$ ,  $3 \text{ min hold}$ ,  $20^\circ \text{C min}^{-1}$  ramp). Eluents were ionized using electron ionization and analysed by an Agilent 5975C mass spectrometer (MS).  $\text{CH}_2\text{ICl}$  and  $\text{CH}_2\text{I}_2$  were measured using  $m/z$  176/178 and 268/254 as quantification/qualification ions, respectively.

Surface seawater was sampled from the ship's seawater inlet, located approx. 2–4 m (depending on sea-state) below the waterline, every 55 min (as well as at various depths from conductivity, temperature, depth (CTD) casts at specific points during the voyage, which are not discussed here). The seawater was pumped through the bow of the ship and through a vortex de-bubbler (Seabird) to remove any air bubbles, at a flow of around  $10 \text{ L min}^{-1}$  through 1/2" PFA tubing. A peristaltic pump was used to divert a portion of the water to an automated purge and trap (AutoP&T) system (Andrews et al. 2015). Briefly, the AutoP&T comprises a heated glass purge vessel automatically filled and emptied using a series of valves. A fixed sample volume ( $20 \text{ mL}$ ) was filtered ( $0.45 \mu\text{m}$ , PTFE filter) and de-gassed at  $50^\circ \text{C}$  using  $1 \text{ L}$  of zero grade nitrogen at  $50 \text{ mL min}^{-1}$ . Analysis was carried out using a second GC-MS with

the same set-up as the air instrument. Similarly to the air measurements, atmospheric  $\text{CCl}_4$  was used to correct for short-term sensitivity changes between calibrations, by rapid sampling of 500 mL of air between each water sample.

### 2.1.2 Ozone measurements

Atmospheric ozone concentrations were measured throughout the cruise using a Thermo Scientific Model 49i Ozone Analyzer. The ozone analyzer was connected to the main air sampling line just downstream of the tee connecting the metal bellows pump.

## 2.2 Sea-air flux determination

Fluxes of VSLH across the ocean-atmosphere interface were calculated from the seawater-air concentration gradients using the two-layer model (Liss and Slater 1974);

$$F = k_T(C_w - C_g/H) \quad (2)$$

and

$$1/k_T = 1/k_w + 1/Hk_a \quad (3)$$

where  $C_w$  and  $C_g$  are the respective bulk water and gaseous concentrations,  $H$  is the dimensionless gas- over-liquid form of the Henry's law coefficient and  $k_T$ ,  $k_w$  and  $k_a$  are the total, liquid and air mass transfer coefficients, respectively. We use the Nightingale et al. (2000) parameterization for  $k_w$ , and for  $k_a$  the parameterization recommended by Johnson (2010). Pure water values of  $H$  from the compilation of Sander (1999) were corrected for salinity using the scheme of Johnson (2010).

## 2.3 THAMO model

The Tropospheric Halogen Chemistry model (THAMO) is a one-dimensional chemistry transport model with 200 stacked boxes at a vertical resolution of 5 m and a total height of 1 km (see Saiz-Lopez et al. 2008). The lowest level is the ocean surface, where gas phase deposition and upward flux can occur. Deposition to a specified aerosol surface area occurs with uptake coefficients taken from the recommendations of Sander et al. (2006) and Atkinson et al. (2000). The chemical scheme used for this study is from Saiz-Lopez et al. (2008) and is updated according to Mahajan et al. (2010a, b).

The modeled data discussed herein are the THAMO results at a height of 10 m above sea level (asl). The injection of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  in the model is constrained by the fluxes measured in the field campaign. Photolysis rate constants for  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  were calculated by an explicit two-stream radiation scheme, which calculates the solar irradiance as a function of altitude, wavelength and solar zenith angle. For these simulations we assumed clear sky conditions. The modelled loss due to dry deposition of these species to the ocean is about 2 %. Measured  $\text{O}_3$  concentrations and assumed ranges of oceanic  $\text{NO}_2$  mixing ratios (see section 3.3) were used to calculate  $\text{NO}_3$  radical concentrations.

## 2.4 Laboratory measurements

Kinetics of the  $\text{NO}_3 + \text{CH}_2\text{I}_2$  reaction were derived from a laboratory study conceived primarily to investigate the reaction between stabilised Criegee intermediates (SCIs) and  $\text{NO}_2$ . Full details are given in Ouyang et al. (2013); briefly, diiodomethane ( $\text{CH}_2\text{I}_2$ ) was photolysed at 248 nm, in the presence of  $\text{NO}_2$  and a bath gas of synthetic air. 248 nm  $\text{CH}_2\text{I}_2$  photolysis is known to lead to the formation of the  $\text{CH}_2\text{OO}$  SCI in the presence of oxygen (Gravestock et al. 2010; Welz et al. 2012), and in turn form  $\text{NO}_3$  as a product of the  $\text{CH}_2\text{OO} + \text{NO}_2$  reaction.  $\text{NO}_3$  formation was monitored by broad-band cavity enhanced absorption spectroscopy (BBCEAS), permitting insight into the  $\text{CH}_2\text{I}_2 + \text{NO}_3$  reaction. Experiments were performed across the accessible experimental conditions (in particular, with regard to precursor abundance), including monitoring  $\text{NO}_3$  abundance as a function of the  $\text{CH}_2\text{I}_2$  concentration, whilst keeping all other aspects constant; these data allow us to constrain the rate constant  $k(\text{NO}_3 + \text{CH}_2\text{I}_2)$ .

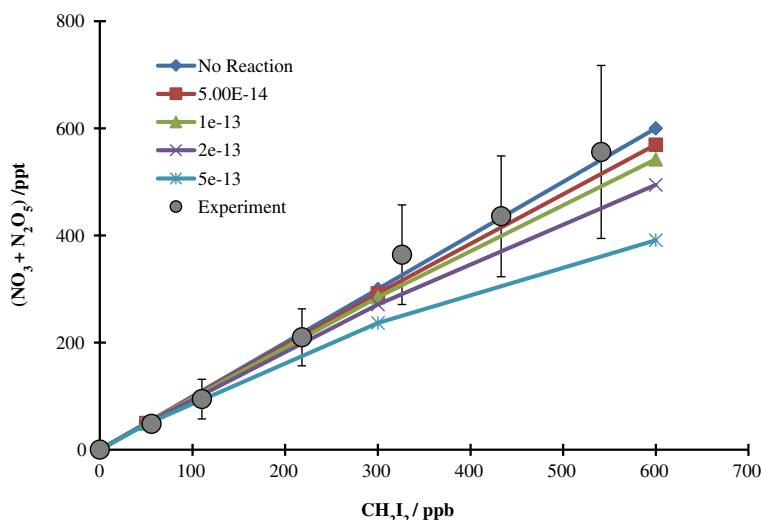
Experiments were performed in an atmosphere of synthetic air at ambient (1 bar) pressure and  $295 \pm 5$  K temperature, with 450 ppb  $\text{NO}_2$  and with the  $\text{CH}_2\text{I}_2$  mixing ratio varied from 56 to 541 ppb. The reagent mixture was continuously flowed through the reaction cell, and photolysed by the 248 nm output from an Excimer laser, expanded and re-collimated to fill the reaction cell, operating at a total power of approximately  $200 \text{ mJ pulse}^{-1}$  (monitored by a calibrated power meter located after the reaction cell), and with a pulse repetition frequency of 0.1 Hz (ensuring total gas replenishment between pulses). The resulting  $\text{NO}_3$  formation was measured by BBCEAS, after a ca. 4 s transit time from the photolysis reactor to the absorption instrument. Owing to the presence of substantial concentrations of  $\text{NO}_2$ , the majority of the  $\text{NO}_3$  was titrated into  $\text{N}_2\text{O}_5$  during the 4 s transit period; the BBCEAS was therefore operated using a heated inlet and absorption cell, to thermally decompose  $\text{N}_2\text{O}_5$  to  $\text{NO}_3 + \text{NO}_2$ . The quantity measured was therefore technically the sum of  $\text{NO}_3 + \text{N}_2\text{O}_5$ , as described in the Results.

## 3 Results

### 3.1 Kinetic data

The measured variation in ( $\text{NO}_3 + \text{N}_2\text{O}_5$ ) with  $\text{CH}_2\text{I}_2$  abundance is shown in Fig. 2. The observed behaviour was compared with the predictions of a simple model, which reproduced the evolution of  $\text{NO}_3$  between the photolysis pulse and the BBCEAS cavity (i.e. through the 4 s transit period), and which incorporated initial  $\text{NO}_3$  production,  $\text{NO}_3/\text{NO}_2/\text{N}_2\text{O}_5$  equilibration, and the reaction of  $\text{NO}_3$  with  $\text{CH}_2\text{I}_2$  to form (unreactive) products. Within the model, the  $\text{NO}_2$  and  $\text{CH}_2\text{I}_2$  concentrations were fixed at their (known) values; standard  $\text{NO}_2/\text{NO}_3/\text{N}_2\text{O}_5$  kinetics were taken from the MCMv3.1 (Bloss et al. 2005), and the initial  $\text{NO}_3$  abundance was calculated based upon the  $\text{CH}_2\text{I}_2$  abundance, laser fluence and SCI yield; a single optimised value of the latter parameter was applied to all simulations. The rate constant for the  $\text{NO}_3 + \text{CH}_2\text{I}_2$  reaction,  $k_1$ , was varied, allowing the predicted variation of ( $\text{NO}_3 + \text{N}_2\text{O}_5$ ) with  $\text{CH}_2\text{I}_2$  concentration to be compared with that observed as shown in Fig. 2. The experimental data clearly show an essentially linear dependence upon  $\text{CH}_2\text{I}_2$ , indicating that the  $\text{NO}_3 + \text{CH}_2\text{I}_2$  reaction has little effect under these (laboratory) conditions. The model data show that values of  $k_1$  in excess of  $5 \times 10^{-13} \text{ molec cm}^{-3}$  are not consistent with the observed behaviour, and we





**Fig. 2** Measured ( $\text{NO}_3 + \text{N}_2\text{O}_5$ ) mixing ratio (filled grey circles, with  $\pm 2 \sigma$  error bars, reflecting combined precision and systematic (uncertainties in the  $\text{NO}_3$  absorption spectrum & fitting) components), compared with model predictions of the variation in ( $\text{NO}_3 + \text{N}_2\text{O}_5$ ) (coloured lines), as a function of  $\text{CH}_2\text{I}_2$ , for different values of  $k_1$  ( $\text{NO}_3 + \text{CH}_2\text{I}_2$ ) in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

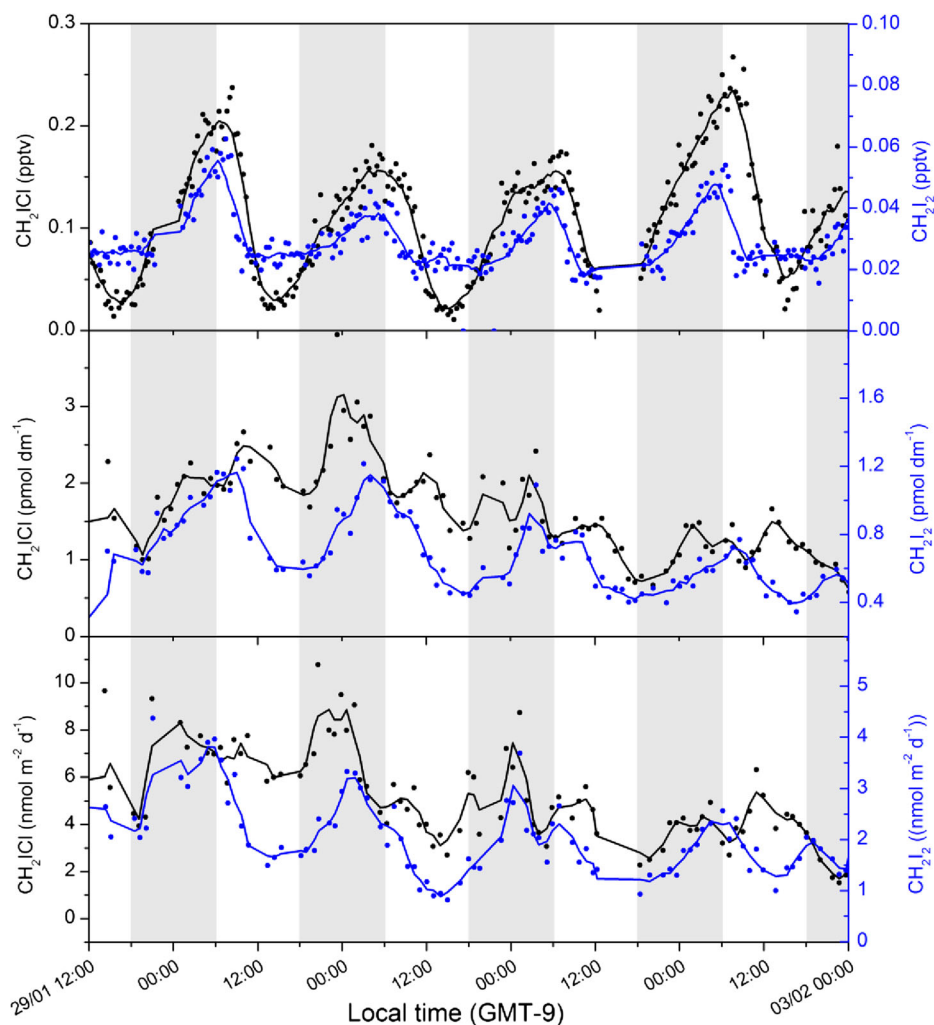
derive an upper limit of  $k_1 \leq 4 \times 10^{-13} \text{ molec cm}^{-3}$ , at 295 K and 1 bar total pressure (i.e. nominal ambient MBL conditions).

### 3.2 Field data

We choose as a case study 4 days of measurements during 29th Jan. – 2nd Feb. 2012 whilst transiting the North Equatorial Current in a southeasterly direction (Fig. 1). This period encountered stable surface chlorophyll *a* concentrations ( $0.1\text{--}0.2 \mu\text{g m}^{-3}$ ), sea surface temperatures (SSTs) ( $24.3 \pm 0.3^\circ\text{C}$ ), wind speeds ( $8.5 \pm 0.8 \text{ ms}^{-1}$ ) and wind direction (Fig. 1), and showed similar daily patterns of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ICl}$  atmospheric and seawater concentrations (Fig. 3).

Both gases displayed notable diurnal cycles in the atmosphere with mixing ratios steadily increasing during the night and rapidly decreasing at sunrise. Mean night-time/early morning maxima and day-time minima were (max:  $0.047 \pm 0.01$ ) pptv and (min:  $0.023 \pm 0.004$ ) pptv for  $\text{CH}_2\text{I}_2$  and (max:  $0.17 \pm 0.03$ ) pptv and (min:  $0.03 \pm 0.01$ ) pptv for  $\text{CH}_2\text{ICl}$ . Thus, the ratio of night-time maxima to day-time minima was more than a factor of two higher for  $\text{CH}_2\text{ICl}$  mixing ratios (average of 5.3) than for  $\text{CH}_2\text{I}_2$  (average of 2.0). This is surprising since the atmospheric photolysis lifetime of  $\text{CH}_2\text{I}_2$  is much shorter than that of  $\text{CH}_2\text{ICl}$ , as discussed in the Introduction. Seawater concentrations also showed diurnal cycles in  $\text{CH}_2\text{I}_2$ , as expected due to its fast photochemical decay in seawater (Jones and Carpenter 2005). Fluxes averaged  $1.8 \pm 0.8 \text{ nmol m}^{-2} \text{ d}^{-1}$  for  $\text{CH}_2\text{I}_2$  and  $3.7 \pm 0.8 \text{ nmol m}^{-2} \text{ d}^{-1}$  for  $\text{CH}_2\text{ICl}$  for the case study period, with night-time fluxes around 2–3 times higher than day-time for  $\text{CH}_2\text{I}_2$  (but only 15 % higher and within the data variability for  $\text{CH}_2\text{ICl}$ ). Thus, in the absence of any night-time loss, nocturnal  $\text{CH}_2\text{I}_2$  mixing ratios should be higher than expected given an assumption of a constant sea-air flux,



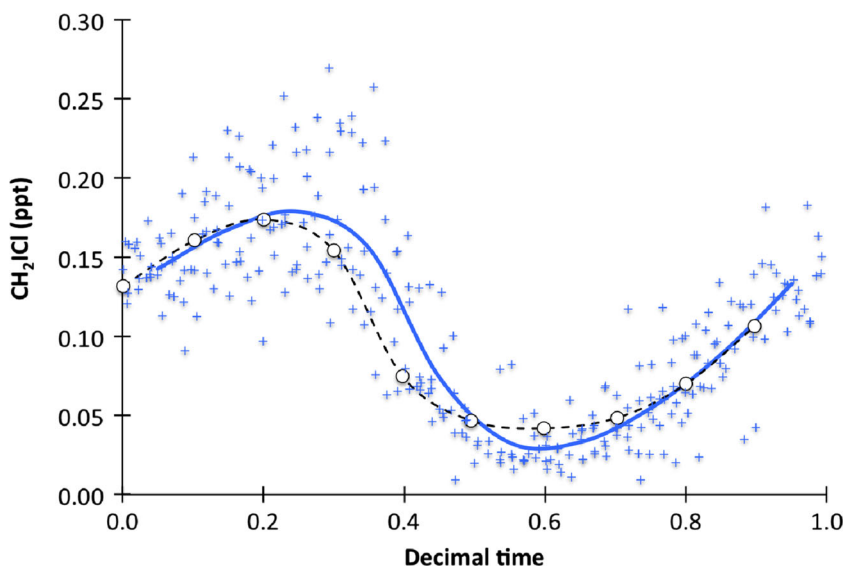


**Fig. 3** Atmospheric mixing ratios, seawater concentrations, and sea-air fluxes of  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{I}_2\text{Cl}$  measured during the TORERO cruise

whereas the reverse is true. Hourly fluxes are used to drive the 1D modeling, so such effects are taken care of in the analysis discussed in the next sections. Together, these results strongly suggest an additional night-time loss of  $\text{CH}_2\text{I}_2$  in the atmosphere.

### 3.3 1D modelling

The THAMO model was used to investigate the effect of reaction (1) on the levels of observed  $\text{CH}_2\text{I}_2$  during the TORERO campaign. Fig. 4 shows that there was no systematic difference between modeled and measured  $\text{CH}_2\text{I}_2\text{Cl}$  mixing ratios, suggesting that the model dynamics and mixing have the required level of skill, and that depositional losses are appropriate. Both the overall  $\text{CH}_2\text{I}_2\text{Cl}$  levels and the diurnal range are simulated well, and no night-time losses of  $\text{CH}_2\text{I}_2\text{Cl}$  are required to reconcile the model output with the observations.



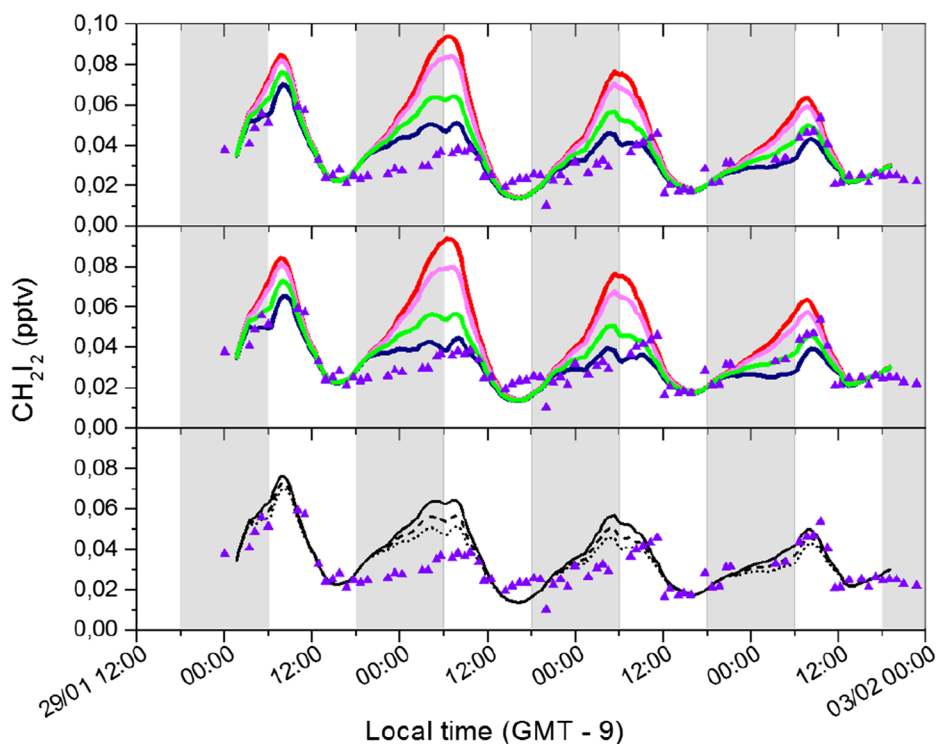
**Fig. 4** Diurnal average  $\text{CH}_2\text{I}_2$  mixing ratios during the period 29th Jan. – 2nd February 2012. Circles and black dotted lines show average of THAMO simulations. Blue crosses are hourly measurements, stripped of day of year. Blue line shows an hourly average of the measurements

Figure 5 shows however that for  $\text{CH}_2\text{I}_2$ , the base model (no  $\text{NO}_3$  reaction) overestimates night-time mixing ratios. On average over this period the model overestimation is a factor of 1.62. Figure 5 also shows the influence of including reaction (1) at different rate constants and  $\text{NO}_2$  (hence  $\text{NO}_3$  radical) concentrations.

Three out of the four days of data are simulated well with  $k_1$  of  $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and 30–40 pptv  $\text{NO}_2$  (corresponding to 14–18 ppt peak  $\text{NO}_3$ ) or  $4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and 20 pptv  $\text{NO}_2$  (corresponding to 9 ppt peak  $\text{NO}_3$ ). On the 31st January the model overestimates average  $\text{CH}_2\text{I}_2$  night-time levels under all the scenarios considered here, although the maximum night-time concentration is simulated well under the highest loss scenario. Without additional measurements we cannot be conclusive on the reasons for this, although higher  $\text{NO}_3$  radical concentrations during this period are a possible explanation. Aircraft measurements made over the eastern Pacific Ocean as part of the NASA GTE/CITE 2 program indicate typical  $\text{NO}_2$  values of  $18 \pm 15$  ppt for maritime tropical air (Carroll et al. 1990) and ~50 ppt has been estimated as an upper limit for the remote ocean boundary layer from MAX-DOAS and satellite (SCIAMACHY and GOME-2) data (Peters et al. 2012).

## 4 Summary and conclusions

Our field data of atmospheric  $\text{CH}_2\text{I}_2$  along with oceanic fluxes calculated from measured seawater concentrations are strongly indicative of a missing night-time sink of  $\text{CH}_2\text{I}_2$ , potentially through reaction with  $\text{NO}_3$  radicals. In the absence of  $\text{NO}_3$  measurements during our field study, it is not possible to infer the  $\text{CH}_2\text{I}_2 + \text{NO}_3$  rate constant with certainty, although a range of  $2\text{--}4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  offers generally good reconciliation between model and measurements. This range is consistent with a laboratory-derived upper limit, presented



**Fig. 5** The influence of different  $k_1$  and  $\text{NO}_2$  mixing ratios on modelled  $\text{CH}_2\text{I}_2$ , compared with measurements. Lines are model results, purple triangles indicate  $\text{CH}_2\text{I}_2$  measurements. Upper panel: 20 ppt  $\text{NO}_2$  at different  $k_1$  (red - no reaction, magenta -  $k_1 = 5 \times 10^{-14}$ , green -  $k_1 = 2 \times 10^{-13}$ , dark blue -  $k_1 = 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ); Middle panel: 30 ppt  $\text{NO}_2$  at different  $k_1$  (lines as before); Lower panel: varying  $\text{NO}_2$  concentrations at  $k_1 = 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (solid line -  $\text{NO}_2 = 20$  ppt, dashed line -  $\text{NO}_2 = 30$  ppt; dotted line -  $\text{NO}_2 = 40$  ppt)

herein, and previous direct measurements made at low pressure. Given the importance of this reaction for understanding the atmospheric behavior of  $\text{CH}_2\text{I}_2$ , we recommend further laboratory measurements of the rate constant and the products of the reaction. Nakano et al. (2006) suggest that the possible products may be the compounds produced from H-transfer and I-transfer reactions:



The available thermodynamic data suggest that channel 1a is favourable but 1b is endothermic (Atkinson et al. 2004; Marshall et al. 2005; Sander et al. 2006), indicating that the reaction  $\text{NO}_3 + \text{CH}_2\text{I}_2$  represents a loss of  $\text{NO}_x$  to  $\text{HNO}_3$ . Further reactions of  $\text{CHI}_2$  and  $\text{CH}_2\text{I}$  are uncertain, although in both cases I atoms are eventually produced which will form IO in the presence of  $\text{O}_3$ . Oxidation of  $\text{CH}_2\text{I}$  (by  $\text{O}_2$ ) leads to the Criegee intermediate  $\text{CH}_2\text{OO}$  along with other products (Gravestock et al. 2010; Stone et al., 2013 and references therein). In locations with high  $\text{CH}_2\text{I}_2$  emissions and sufficient  $\text{NO}_3$ , such as polluted coastlines, the

reaction may result in production of nighttime IO, or at least in modification of the diurnal profile of IO.

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## References

- Alicke B., Hebestreit K., Stutz J., Platt U.: Iodine oxide in the marine boundary layer. *Nature*. **397**, 572–573 (1999)
- Andrews, SJ, Hackenberg, SC, Carpenter, LJ.: Technical note: a fully automated purge and trap GC-MS system for quantification of volatile organic compound (VOC) fluxes between the ocean and atmosphere. *Ocean Sci.* **11**: pp. 1–9 (2015). doi:[10.5194/os-11-1-2015](https://doi.org/10.5194/os-11-1-2015)
- Atkinson R., Baulch D.L., Cox R.A., Crowley J.N., Hampson J., Hynes R.G., Jenkin M.E., Kerr J.A., Rossi M.J., Troe J.: Summary of evaluated kinetic and photochemical data for atmospheric chemistry. IUPAC. *J. Phys. Chem. Ref. Data*. **29**, 167–266 (2000)
- Atkinson R., Baulch D.L., Cox R.A., Crowley J.N., Hampson J., Hynes R.G., Jenkin M.E., Kerr J.A., Rossi M.J., Troe J.: Evaluated kinetic and photochemical data for atmospheric chemistry: volume I - gas phase reactions of ox, HOx, NOx and SOx species. *Atmos. Chem. Phys.* **4**, 1461–1738 (2004)
- Bloss, C, Wagner, V, Jenkin, ME, Wirtz, K, Wenger, J, Bloss, WJ, Lee, JD, Heard, DE, and Pilling MJ (2005) Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. *Atmos. Chem. Phys.* **5**: pp. 641–664.
- Carpenter L.J., Sturges W.T., Penkett S.A., Liss P.S., Alicke B., Hebestreit K., Platt U.: Short-lived alkyl iodides and bromides at mace head, Ireland: links to biogenic sources and halogen oxide production. *J. Geophys. Res.* **104**(D1), 1679–1689 (1999)
- Carpenter L.J., MacDonald S.M., Shaw M.D., Kumar R., Saunders R.W., Parthipan R., Wilson J., Plane J.M.C.: Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine. *Nat. Geosci.* **6**, 108–111 (2013). doi:[10.1038/ngeo1687](https://doi.org/10.1038/ngeo1687)
- Carpenter, LJ, Reimann, S, Burkholder, JB, Clerbaux, C, Hall, BD, Hossaini, R, Laube, JC, Yvon-Lewis, SA.: Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol: Chapter 1 in Scientific Assessment of Ozone Depletion: 2014, Global ozone research and monitoring project – report no. 55, World Meteorological Organization, Geneva (2014)
- Carroll M.A. et al.: Aircraft measurements of NO<sub>x</sub> over the eastern Pacific and continental United States and implications for ozone production. *J. Geophys. Res.* **95**, 10,205–10,233 (1990)
- Chameides W.L., Davis D.: Iodine: its possible role in tropospheric photochemistry. *J. Geophys. Res.* **85**, 7383–7398 (1980)
- Dix B., Baidar S., Bresch J.F., Hall S.R., Schmidt K.S., Wang S., Volkamer R.: Detection of iodine monoxide in the tropical free troposphere. *P. Natl. Acad. Sci. USA*. **110**, 2035–2040 (2013). doi:[10.1073/pnas.1212386110](https://doi.org/10.1073/pnas.1212386110)
- Gómez Martín J.C., Mahajan A.S., Hay T.D., Prados-Román C., Ordóñez C., MacDonald S.M., Plane J.M.C., Sorribas M., Gil M., Paredes Mora J.F., Agama Reyes M.V., Oram D.E., Leedham E., Saiz-Lopez A.: Iodine chemistry in the eastern Pacific marine boundary layer. *J. Geophys. Res.-Atmos.* **118**, 887–904 (2013). doi:[10.1002/jgrd.50132](https://doi.org/10.1002/jgrd.50132)
- Gravestock T.J., Blitz M.A., Bloss W.J., Heard D.E.: A multidimensional study of the reaction CH<sub>2</sub>I + O<sub>2</sub>: products and atmospheric implications. *Chem. Phys. Chem.* **11**, 3928–3941 (2010)
- Großmann K., Frieß U., Peters E., Wittrock F., Lampel J., Yilmaz S., Tschritter J., Sommariva R., von Glasow R., Quack B., Krüger K., Pfeilsticker K., Platt U.: Iodine monoxide in the western Pacific marine boundary layer. *Atmos. Chem. Phys.* **13**, 3363–3378 (2013). doi:[10.5194/acp-13-3363-2013](https://doi.org/10.5194/acp-13-3363-2013)
- Johnson M.T.: A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas. *Ocean Sci.* **6**, 913–932 (2010)

- Jones C.E., Carpenter L.J.: Solar photolysis of  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{ICl}$ , and  $\text{CH}_2\text{IBr}$  in water, saltwater, and seawater. *Environ. Sci. Technol.* **39**, 6130–6137 (2005)
- Jones, CE, Hornsby, KE, Sommariva, R, Dunk, RM, von Glasow, R, McFiggans, G, Carpenter, L.J.: Quantifying the contribution of marine organic gases to atmospheric iodine. *Geophys. Res. Lett.* **37**: L18804 (2010).
- Liss P.S., Slater P.G.: Flux of gases across the air-sea interface. *Nature*. **247**, 181–184 (1974)
- MacDonald S.M., Gómez Martín J.C., Chance R., Warriner S., Saiz-Lopez A., Carpenter L.J., Plane J.M.C.: A laboratory characterisation of inorganic iodine emissions from the sea surface: dependence on oceanic variables and parameterisation for global modeling. *Atmos. Chem. Phys.* **14**, 5841–5852 (2014)
- Mahajan A.S., Plane J.M.C., Oetjen H., Mendes L., Saunders R.W., Saiz-Lopez A., Jones C.E., Carpenter L.J., McFiggans G.B.: Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic ocean. *Atmos. Chem. Phys.* **10**, 4611–4624 (2010a). doi:10.5194/acp-10-4611-2010
- Mahajan, AS, Shaw, M, Oetjen, H, Hornsby, KE, Carpenter, LJ, Kaleschke, L, Tian-Kunze, X, Lee, JD, Moller, SJ, Edwards, P, Commane, R, Ingham, T, Heard, DE, Plane, JMC.: Evidence of reactive iodine chemistry in the Arctic boundary layer. *J. Geophys. Res.*, **115**: D20303, (2010b). doi: 10.1029/2009JD013665
- Marshall P., Srinivas G.N., Schwartz M.: A computational study of the thermochemistry of bromine- and iodine-containing methanes and methyl radicals. *J. Phys. Chem. A*. **109**, 6371–6379 (2005)
- Martino M., Liss P.S., Plane J.M.C.: The photolysis of dihalomethanes in surface seawater. *Environ. Sci. Technol.* **39**(18), 7097–7101 (2005)
- Mössinger J., Shallcross D.E., Cox R.A.: UV–VIS absorption cross-sections and atmospheric lifetimes of  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{BrI}$ . *J. Chem. Soc. Faraday Trans.* **94**, 1391–1396 (1998)
- Nakano Y., Ukeguchi H., Ishiwata T.: Rate constant of the reaction of  $\text{NO}_3$  with  $\text{CH}_2\text{I}_2$  measured with use of cavity ring-down spectroscopy. *Chemical Physics Letters*. **430**, 235–239 (2006). doi:10.1016/j.cplett.2006.09.002
- Nightingale P.D. et al.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Glob. Biogeochem. Cycles*. **14**, 373–387 (2000)
- Ouyang B., McLeod M.W., Jones R.L., Bloss W.J.:  $\text{NO}_3$  radical production from the reaction between the cregee intermediate  $\text{CH}_2\text{OO}$  and  $\text{NO}_2$ . *Phys. Chem. Chem. Phys.* **15**, 17070–17075 (2013)
- Peters E., Wittrock F., Großmann K., Frieß U., Richter A., Burrows J.P.: Formaldehyde and nitrogen dioxide over the remote western Pacific Ocean: SCIAMACHY and GOME-2 validation using ship-based MAX-DOAS observations. *Atmos. Chem. Phys.* **12**, 11179–11197 (2012). doi:10.5194/acp-12-11179-2012
- Prados-Roman C., Cuevas C.A., Hay T., Fernandez R.P., Mahajan A.S., Royer S.J., Galí M., Simó R., Dachs J., Großmann K., Kinnison D.E., Lamarque J.F., Saiz-Lopez A.: Iodine oxide in the global marine boundary layer. *Atmos. Chem. Phys.* **15**, 583–593 (2015)
- Rattigan O.V., Shallcross D.E., Cox R.A.: UV absorption cross-sections and atmospheric photolysis rates of  $\text{CF}_3\text{I}$ ,  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$  and  $\text{CH}_2\text{ICl}$ . *J. Chem. Soc. Faraday Trans.* **93**, 2839–2846 (1997)
- Read K.A., Mahajan A.S., Carpenter L.J., Evans M.J., Faria B.V.E., Heard D.E., Hopkins J.R., Lee J.D., Moller S., Lewis A.C., Mendes L., McQuaid J.B., Oetjen H., Saiz-Lopez A., Pilling M.J., Plane J.M.C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic ocean. *Nature*. **453**(7199), 1232–1235 (2008)
- Roehl C.M., Burkholder J.B., Moortgat G.K., Ravishankara A.R., Crutzen P.J.: Temperature dependence of UV absorption cross sections and atmospheric implications of several alkyl iodides. *J. Geophys. Res.* **102**, 12819–12829 (1997)
- Saiz-Lopez A., Plane J.M.C., Mahajan A.S., Anderson P.S., Bauguutte S.J.B., Jones A.E., Roscoe H.K., Salmon R.A., Bloss W.J., Lee J.D., Heard D.E.: On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for  $\text{O}_3$ ,  $\text{HO}_x$ ,  $\text{NO}_x$  and the Hg lifetime. *Atmos. Chem. Phys.* **8**, 887–900 (2008). doi: 10.5194/acp-8-887-2008
- Saiz-Lopez A., Fernandez R.P., Ordóñez C., Kinnison D.E., Gómez Martín J.C., Lamarque J.-F., Tilmes S.: Iodine chemistry in the troposphere and its effect on ozone. *Atmos. Chem. Phys.* **14**, 13119–13143 (2014)
- Sander, R.: Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (version 3), <http://www.mpchmainz.mpg.de/~sander/re/henry.html>. (1999)
- Sander S.P., Friedl R.R., Ravishankara A.R., Golden D.M., Kolb C.E., Kurylo M.J., Huie R.E., Orkin V.L., Molina M.J., Moortgat G.K., Finlayson-Pitts B.J.: Chemical kinetics and photochemical data for use in atmospheric studies, evaluation number 14. Administration, Jet Propulsion Laboratory and National Aeronautics and Space (2006)
- Sherwen T., Evans M.J., Carpenter L. J., Andrews S. J., Lidster R. T., Dix B., Koenig T. K., Volkamer R., Saiz-Lopez A., Prados-Roman C., Mahajan A. S., Ordóñez C., Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem, *Atmos. Chem. Phys. Discuss.* **15**, 20957–21023 (2015)
- Stone D., Blitz M., Daubney L., Ingham T., Seakins P.:  $\text{CH}_2\text{OO}$  Criegee biradical yields following photolysis of  $\text{CH}_2\text{I}_2$  in  $\text{O}_2$ . *Phys. Chem. Chem. Phys.* **15**, 19119–19124 (2013)
- Welz O., Savee J.D., Osborn D.L., Vasu S.S., Percival C.J., Shallcross D.E., Taatjes C.A.: Direct Kinetic Measurements of Criegee Intermediate ( $\text{CH}_2\text{OO}$ ) Formed by Reaction of  $\text{CH}_2\text{I}$  with  $\text{O}_2$ . *Science*. **335**, 204 (2012)